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Seasonal Variation of the Physico-chemical Composition of Ottawa River Waters in the St. Lawrence River

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Abstract

The goal of this study is to compare the seasonal variability of 12 physicochemical characteristics of waters in the Ottawa and St. Lawrence Rivers (SLR). Water samples were collected on board the research vessel *Lampsillis* in the spring (May), summer (August), and fall (October) of 2006 at four stations located downstream from the confluence of the two rivers. Temperature and total nitrogen values varied significantly for the three seasons. In contrast, seasonal values of light extinction coefficient and turbidity do not show any significant variation. The values of the other characteristics varied significantly only for one season. Comparison of these data with those measured in 1994–1996 reveals a net warming of the waters and a significant increase in nitrite-nitrate concentrations due to the increasing use of nitrogen-bearing fertilizers by farmers in Quebec. Concentrations of these two substances are higher than the limits set by the government of Quebec for water quality in rivers.

Keywords: physicochemical characteristics, seasons, ANOVA, Kruskal-Wallis test, Ottawa River, St. Lawrence River

1. Introduction

The St. Lawrence River (SLR) forms a complex system composed of a mosaic of heterogeneous zones such as fluvial lakes, connecting reaches and wetlands, which interact with inflowing tributaries to produce strong longitudinal and lateral connectivity between aquatic and terrestrial environments (reviewed in [1]). The tributaries flow through a watershed covering 1,600,000 km², where land use is dominated by a high degree of urbanization near Montreal

and areas of agriculture, pasture, forests, and wetland in the mid- and lower reaches of the stream system [2, 3]. Water intrusions from tributaries contribute to the formation of several parallel water masses with distinct physical and chemical properties. Among these, the Ottawa River plays a significant role in structuring the biogeochemical properties of the brown water river considering its strong discharge rate and largely human impacted watershed [4].

Many studies have analyzed the physicochemical and biological characteristics of these waters (e.g., [5–24]) and of related sediments [25–28], while other studies focused on optical characterization of these waters (e.g., [27–32]). Most of these studies analyzed the spatial variability of these characteristics in the St. Lawrence River, but very few looked at their seasonal and inter-annual variability. One notable exception [12] compared the interannual variability of these characteristics measured upstream and downstream from the confluence of the Ottawa and St. Lawrence Rivers from May through September, from 1994 to 1996. However, the changes in physicochemical characteristics of Ottawa River waters flowing through the St. Lawrence River were not specifically studied at the seasonal or decadal level. The main goal of this study is to analyze the seasonal variability in physical and chemical properties of the Ottawa River water mass flowing in the St. Lawrence River along 80 km further downstream from the confluence. Water characteristics were measured at four stations in the spring (May), summer (August), and fall (October) of 2006, something that has never been analyzed. The secondary goal of the study is to compare these characteristics with those measured 10 years earlier by [12].

2. Description of the Ottawa River watershed

The Ottawa River, which is the main tributary of the St. Lawrence River, takes its source in Lac Capimitchigama (**Figures 1 and 2**). Stretching over approximately 1130 km, the Ottawa drains a 146,334 km² watershed. From a geological standpoint, the river flows mainly through the Canadian Shield, which comprises Archean and/or Proterozoic igneous rocks, as well as Proterozoic metasedimentary and intrusive rocks. Upstream of its confluence with the St. Lawrence River, the Ottawa River flows through the relatively flat St. Lawrence Lowlands, comprising carbonate and siliciclastic sedimentary rocks. Climate in the watershed is cool continental temperate, characterized by very cold and snowy winters and warm and relatively dry summers. Temperatures and precipitations decrease from south to north in the watershed. From a hydrographic standpoint, 19 main tributaries flow into the Ottawa River, of which the primary ones are the Gatineau, Lièvre, Kipawa, Rouge, Madawaska, Montreal, Blanche, and Petawawa. The Ottawa River watershed also includes over 90,000 small and large lakes.

The Ottawa River and most of its tributaries are heavily regulated, the watershed comprising more than 1000 small and large dams, in addition to 30 large reservoirs built to control flood flows. Reservoirs built in the upper reaches of the watershed have inverted the annual cycle of flows such that maximum flows occur in winter and minimum flows in springtime during snowmelt, contrary to the annual flow regime in natural rivers. This inversion, however, fades gradually in the lower reaches of the watershed due to input from natural tributaries (**Figure 3**). Annual mean discharge in the Ottawa River at its confluence with the St. Lawrence River is roughly 1980 m³/s [12], and the watershed is almost completely covered by forests

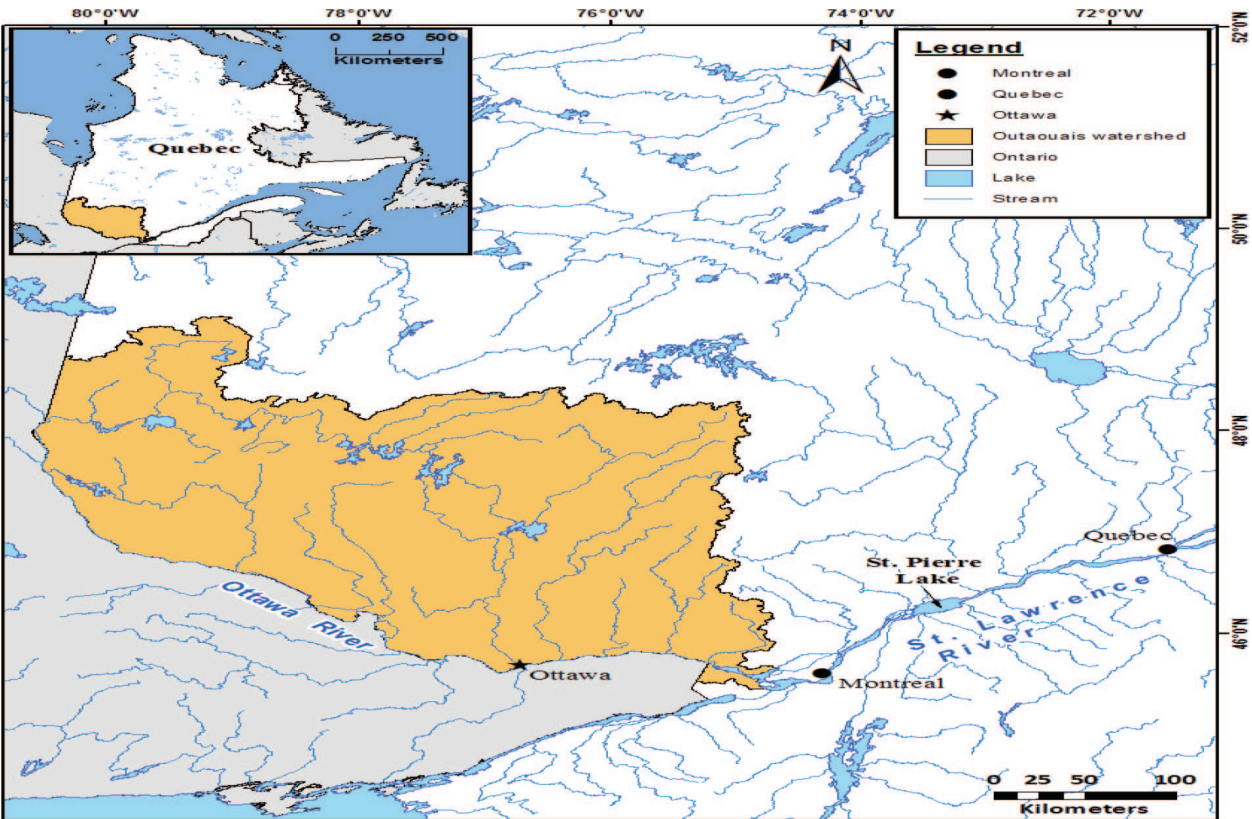


Figure 1. Location of the Ottawa River watershed and the St. Lawrence River.

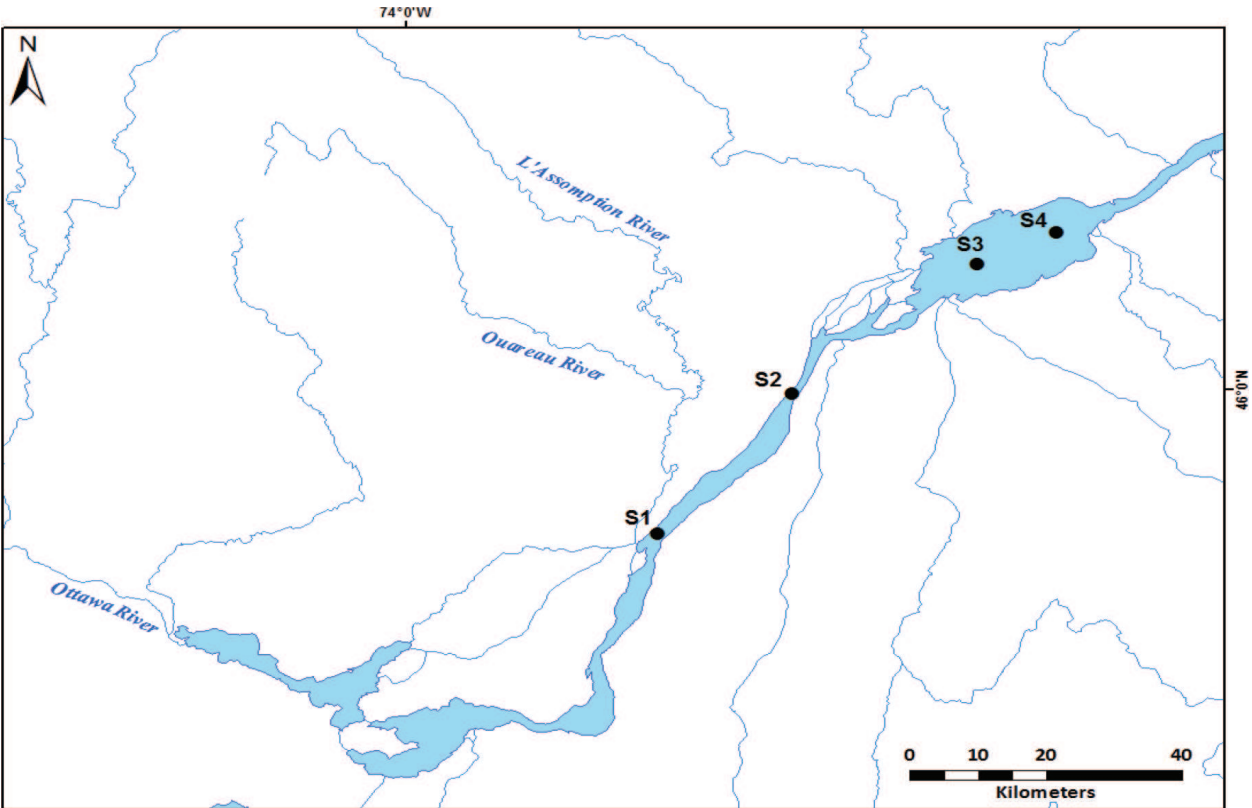


Figure 2. Location of sampling stations along the St. Lawrence River.

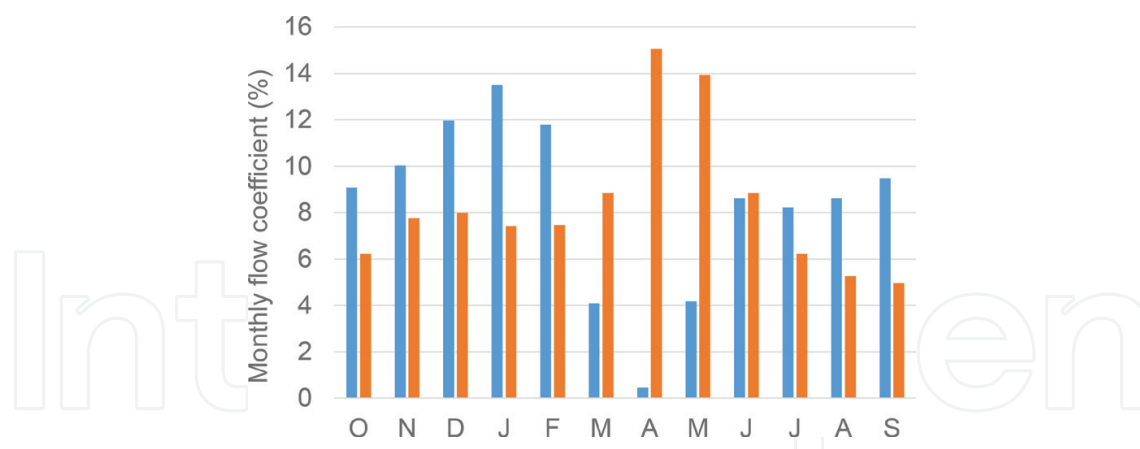


Figure 3. Monthly flow coefficients downstream from the Dozois reservoir (blue bars, 8210 km²) and the Carillon dam (red bars, 143,000 km²) built on the main branch of the Ottawa River.

(deciduous, mixed, and boreal). Farming is only practiced in the lower part of the watershed and accounts for only 3% of its total surface area. The main urban areas in the watershed are the Ottawa-Gatineau and Laval areas.

3. Analysis of the chemical and physical variables of waters

Three 8-day sampling cruises were conducted in the St. Lawrence River (SLR) during spring (23–30 May), summer (9–15 August), and fall (11–17 October) 2006 aboard the RV “Lampsilis” from the Université du Québec à Trois-Rivières. We studied the SLR along a 450 km distance from its source at the outlet of the Great Lakes, until the interface with marine waters at the estuarine transition zone (ETZ), 50 km downstream from the marine intrusion (**Figure 1**). Water samples were collected at the surface (0.5–1.3 m) for all stations using a Go-Flow bottle (8 L) and immediately processed in the wet laboratory after collection.

Sampling was carried out at four stations in the water mass entering from the Ottawa River along 80 km downstream transect (**Figure 2**). At each site, water was subsampled directly in acid-washed bottles for total phosphorus (TP) and total nitrogen (TN) measurements. For soluble reactive phosphorous (PO_4) and for nitrites (NO_2) and nitrates (NO_3), samples were filtrated on 45 mm diameter, 0.7 μm poresize GFF filters (Millipore). PO_4 was analysed using the acid molybdate technique. NO_3 was first reduced into NO_2 by cadmium, and the nitrite concentrations were determined by the sulfanilamide method.). TP and TN concentrations (check) were obtained using the spectrophotometric determination of phosphates and nitrates after digestion by potassium persulfate. All phosphorus and nitrogen analyses were performed according to the American Public Health Association protocols [33]. We used a multiprobe depth profiler (YSI, model 6600EDS-M, YellowSpring Inc.) to measure the conductivity, temperature, and turbidity of the water column. Values for the surface of the water column were averaged between 0.5 and 1.5 m. Physicochemical variables or characteristics of St. Lawrence River waters analyzed as part of this study are presented in **Table 1**.

Variables	May (M1)	August (M2)	October (M3)	Results of comparison of mean values
Temperature (°C)	12.9 (0.78)	23.3 (0.21)	13.9 (0.17)	M1 ≠ M2 ≠ M3
Total nitrogen (TN, mg/L)	4.52 (2.47)*	3.05 (0.70)*	0.70 (0.33)*	M1 ≠ M2 ≠ M3
Nitrite (NO ₂ , mg/L)	9.19 (2.93)*	0.008 (0.003)	1.79 (0.53)*	M1 ≠ (M2 = M3)
Total phosphorous (TP, µg/L)	61.60 (30.89)*	23.47 (12.21)	8.65 (3.17)	M1 ≠ (M2 = M3)
<i>a</i> CDOM _{340nm} (m ⁻¹)	15.79 (5.75)	7.92 (1.65)	3.11 (1.35)	M1 ≠ (M2 = M3)
Nitrate (NO ₃ , mg/L)	0.53 (0.43)*	0.73 (0.21)*	0.55 (0.40)*	M2 ≠ (M1 = M3)
Phosphate (PO ₄ , µg/L)	5.24 (1.03)	10.29 (1.89)	2.20 (1.99)	M2 ≠ (M1 = M2)
Transmittance (trans, %)	24.43 (19.19)	63.28 (8.88)	79.04 (1.11)	M2 ≠ (M1 = M3)
Conductivity (cond, µS/cm)	0.062 (0.019)	0.072 (0.009)	269.0 (4.65)	M3 ≠ (M1 = M2)
Light extinction coefficient ((K _{d(PAR)}) m ⁻¹)	2.46 (0.38)	1.81 (0.23)	0.97 (0.103)	(M1 = M2 = M3)
Turbidity (TURB, NTU)	9.41 (4.13)*	9.39 (6.80)*	4.47 (1.37)*	(M1 = M2 = M3)

(M1≠ M2≠ M3): mean values are significantly different at the 5% level (all statistical tests used).

(M1=M2): mean values are not significantly different at the 5% level (all statistical tests used). (0.78) = standard deviation.

*The mean concentration exceeds the provincial standard limit value.

Table 1. Comparison of seasonal mean values of physicochemical variables measured at four stations in St. Lawrence River water influences by the Ottawa River in 2006.

As far as *a*CDOM measurements, water samples for the absorption coefficient of chromophoric dissolved organic matter (*a*CDOM) and DOC were filtered through Milli-Q-rinsed 0.22 µm Isopore membrane (millipore) and stored them in the dark at 4°C until analysis. We measured CDOM absorption spectra in a 10 mm quartz cell at 1 nm intervals between 190 and 900 nm using a spectrophotometer (Shimadzu UV-2401PC) referenced against Milli-Q water. We used absorbance at 690 nm (where the temperature dependency is near zero) to correct the UV absorption values. We converted absorbance values at 340 nm to absorption coefficients (*a*CDOM_{340nm}) using the following equation [8]:

$$aCDOM_{340nm} = \frac{2.303A_{340nm}}{L} \quad (1)$$

where *L* is the cuvette path length (0.01 m).

As far as spectral radiation and beam attenuation measurements are concerned, photosynthetically available radiation (PAR) (400–700 nm) in the water column was measured at each station as in [1]. Briefly, downward irradiance was measured at every 0.02 m with a spectroradiometer (Model Hyperpro, Satlantic Instruments), which was slowly lowered through the water column to measure depth profiles of the cosine-corrected downwelling under-water irradiance (*E_d*) at every 3 nm between 351 and 750 nm (100 wavebands). Light data were corrected automatically for “dark irradiance” values obtained from the shutter darks.

Diffuse attenuation coefficients ($K_{d(\text{PAR})}$) were calculated by linear regression of the natural logarithm of E_d versus depth. E_d values correspond to PAR. The Hyperpro was equipped with a C-star transmissometer (Wet Labs Inc., 25 cm path length, $\lambda = 660$ nm) to measure depth profiles of the scattering of underwater particles (trans) such as sediments.

Statistical analysis consisted of comparing seasonal mean values of physicochemical variables measured at the four stations using the analysis of variance approach when the data were normal and the Kruskal-Wallis test when the data were not. The same statistical tests were used to compare mean values of certain characteristics at the decadal scale and those of seasonal water levels. Water level data for the St. Lawrence River, taken from the Environment Canada website (https://eau.ec.gc.ca/download/index_f.html?results_type=historical, viewed on September 20, 2017) and measured at the Lanoraie station (ID: 02OB011; 45°57'33" N, 73°15'52" W) since 1990, are strongly influenced by water masses entering from the Ottawa River.

4. Results and discussion

4.1. Seasonal variability

In order to characterize the 2006 hydrological year, water levels measured in the St. Lawrence River in 2006 were compared with mean water levels derived for a 20-year period (1990–2010) at the Lanoraie station (**Figure 4**). For the 3 months during which sampling was done, mean water levels were higher than the 20-year calculated mean for the months of May and October 2006 but equal for the month of August.

A comparison of seasonal mean values of physicochemical variables reveals that mean values of temperature and total nitrogen (TN) are significantly different for the three seasons

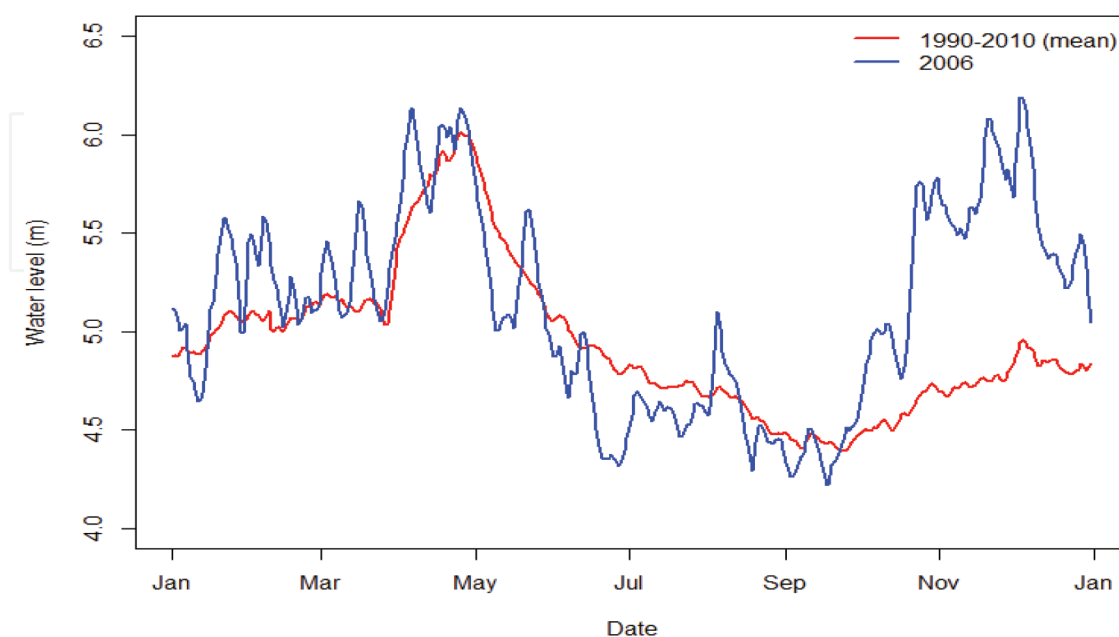


Figure 4. Comparison of daily water levels in the St. Lawrence River measured in 2006 (blue curve) and daily mean values calculated over the period from 1990 to 2010 (red curve) at the Lanoraie station.

(Table 1 and Figure 5). As far as temperature is concerned, it is higher in August (summer) than in May (influence of snowmelt water) and October (effect of fall cooling). In summer, water temperature is roughly twice as high as in the spring or fall due to low water levels (low flow) and the increase in solar energy. TN, for its part, which is mainly derived from farming in Quebec, decreases from spring to fall. In springtime, there is widespread runoff on slopes due to snowmelt, which accounts for the increase in TN concentration in rivers. This concentration decreases in summer as runoff decreases. However, because of the relatively low water levels, the total nitrogen concentration remains higher than in the fall due to limited dilution. In any case, mean TN concentrations during the three seasons are higher than the provincial standard limit value (0.5 mg/L).

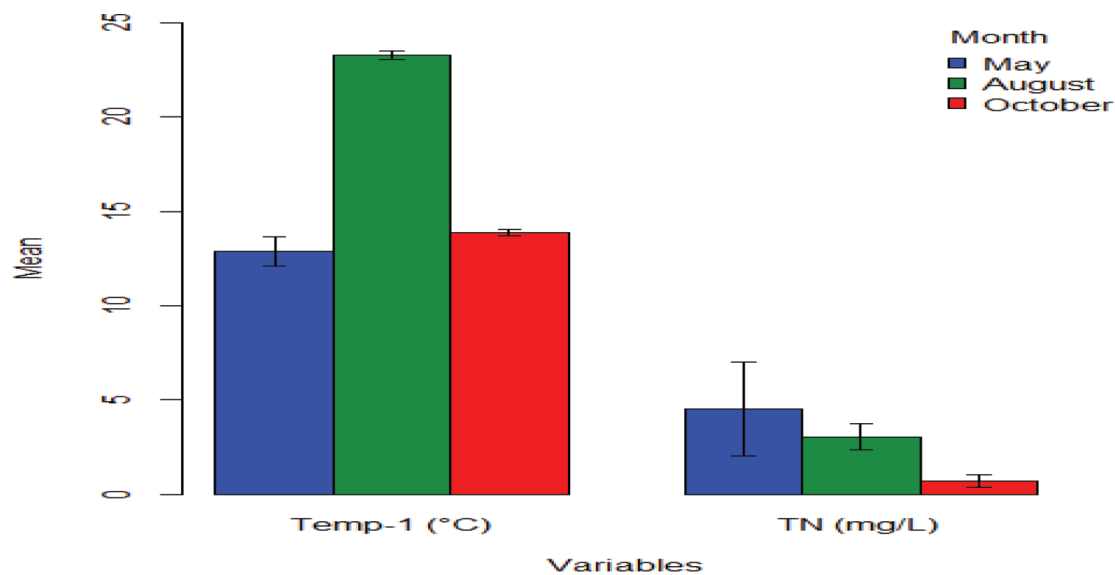


Figure 5. Comparison of seasonal mean values of temperature and TN.

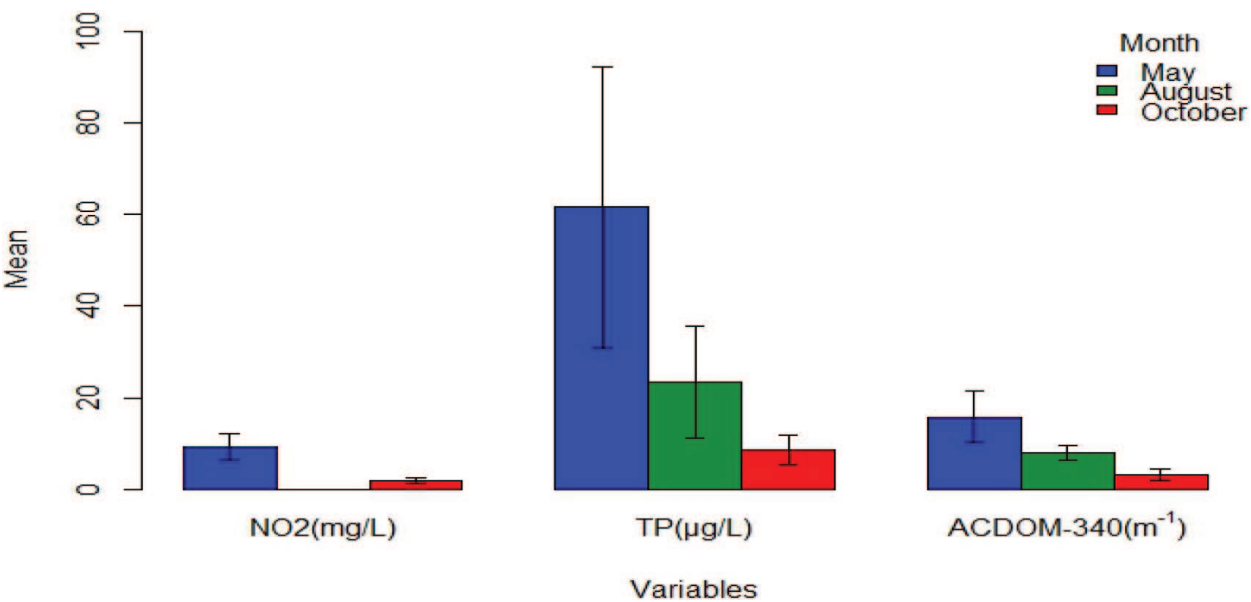


Figure 6. Comparison of seasonal mean values of NO₂, TP and _aCDOM_{340nm}.

Mean values of six physicochemical variables are significantly different during two seasons. Nitrite (NO_2), total phosphorus (TP), and chromophoric organic matter ($a\text{CDOM}_{340\text{nm}}$) concentrations are higher in springtime than in the other two seasons (**Figure 6**). This springtime increase is thought to be due to flushing induced by runoff of snowmelt water and resulting in leaching of terrestrial organic and inorganic material. In the case of nitrate (NO_3) and soluble reactive phosphorus (PO_4), their concentrations are higher in summer than in the other two seasons due to limited dilution during the low-flow period and runoff water during summer storm events (**Figure 7**). These two factors can also account for the high values of suspended particles (trans-variable) observed in summer. As for conductivity, its mean value increases markedly in the fall. As far as total phosphorus is concerned, its spring concentration is much higher than the standard limit set by the Ministère de l'Environnement du Québec [34], whereas NO_3 concentrations exceed the standard limit for all three seasons. Mean values of the two other variables ($(K_{\text{d(PAR)}}) \text{ m}^{-1}$) and TURB) do not show significant seasonal variations (**Figure 8**). Turbidity values are higher than the provincial standard limit (1NTU) for the three seasons.

4.2. Decadal variability

Mean values of physicochemical variables measured in 2006 were compared with those measured in 1994–1996 by [12] in waters of the St. Lawrence River influenced by the Ottawa River (**Table 2**). Hydrological conditions are similar for the two periods because mean water levels in the St. Lawrence River from May to October are not significantly different. A clear warming of the water is observed between 1994 and 1996 and 2006, as well as a significant increase in nitrite-nitrate concentrations due to climate warming, increased use of nitrogen fertilizers, spreading of solid and liquid manure, as well as effluent releases. In contrast, the amount of phosphate decreased significantly from 1994 to 1996 to 2006 due to its decreasing concentrations in effluents from water treatment plants [34].

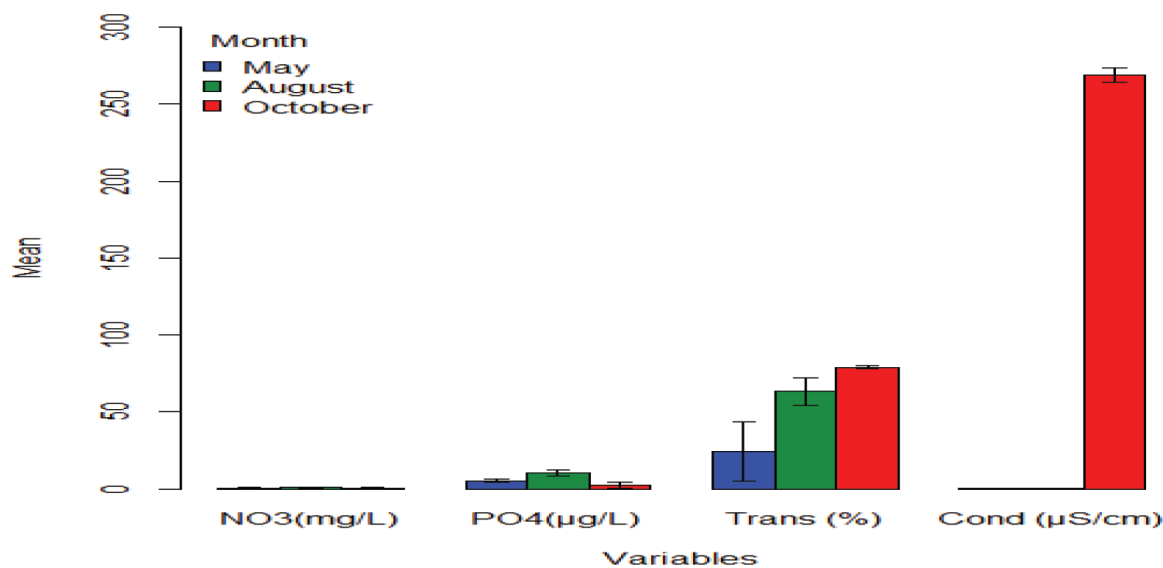


Figure 7. Comparison of seasonal mean values of NO_3 , PO_4 , transmittance and conductivity.

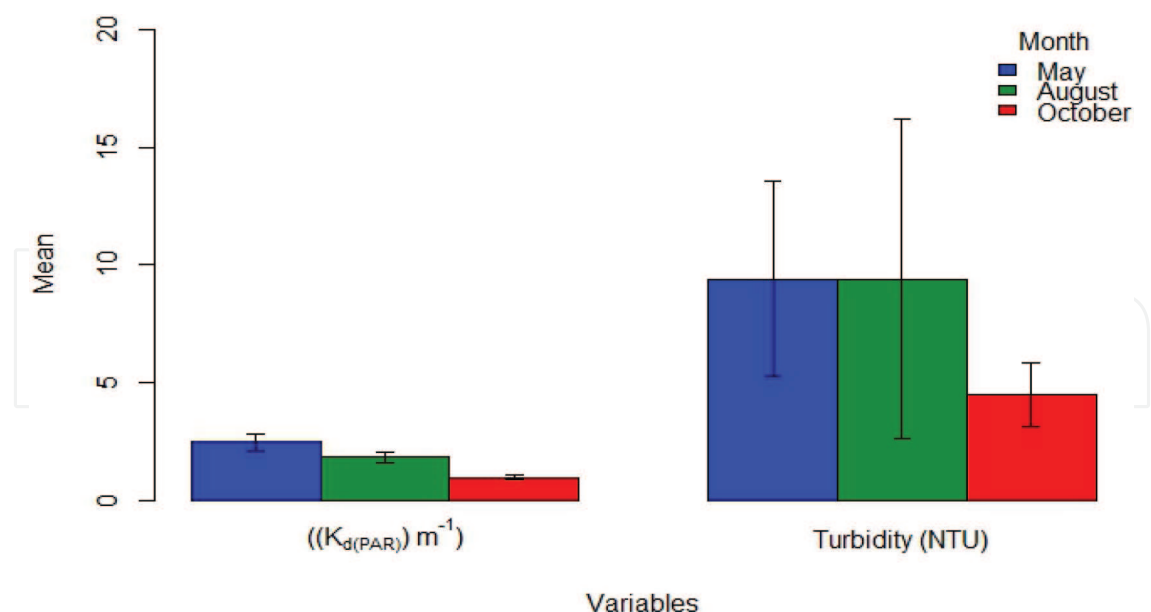


Figure 8. Comparison of seasonal mean values of $K_{d(PAR)}$ and TURB variables.

Variables	1994–1996*	2006
Water level (m) [§]	4.91 (0.39)	4.78 (0.40)
Temperature (°C)	13.2 (7.9)	16.7 (4.89)
Conductivity (µS/cm)	124 (24)	89.7 (132.46)
Light extinction coefficient ($((K_{d(PAR)}) m^{-1})$)	1.80 (0.45)	1.75 (0.68)
NO ₂ -NO ₃ (mg/L)	0.35 (0.25)	2.75 (2.13)
PO ₄ (mg/L)	0.018 (0.007)	0.0059 (0.0038)

() = standard deviation.*Data published by [12].

[§]Water levels measured at the Lanoraie station.

Table 2. Comparison of mean concentrations of some physicochemical variables in Ottawa River waters in the St. Lawrence River measured from May to October in 1994–1996 and 2006.

Watershed and water resource management strategies are currently applied in the context of global warming and therefore, cannot be interrupted by the implementation of a new regulation program at the provincial and/or federal level. However, the monitoring of potential negative impacts of global warming on the other components of the river ecosystem (plants, animals, water quality, etc.) would allow the quantification of the environmental damages and the implementation of regulation to protect river ecosystems. Such a regulation would enable the development of appropriate mitigation procedures to minimize dramatic environmental consequences. It is important to note the low number of environmental studies on Québec Rivers and, more specifically, the urgent need for studies devoted to the impacts of global warming on river ecosystems. Without such environmental monitoring, it becomes

difficult to predict the evolution of river ecosystems in the context of global warming. The observed increase in nitrites-nitrates in the last 10 years reinforces the need for the Québec Government to develop an efficient management program which would significantly reduce the massive nitrogen fertilizer inputs in agriculture. In addition, this management program should include the respect of legal water quality standards for nitrogen wastes in rural and city areas. These standards already exist but are barely applied.

5. Conclusion

As already pointed out by Hudon [12], flow variations exert a strong influence on the physico-chemical characteristics of Ottawa River waters. This influence was observed in St. Lawrence River waters affected by the Ottawa River. However, this influence does not affect all characteristics in the same way. Depending on this influence, these characteristics may be grouped into three categories. The first category comprises water temperature and total nitrogen, the values of which vary seasonally as a function of water levels. The second category comprises variables that vary significantly over a single season, resulting in marked increases in the spring (NO_2^- , TP, $a\text{CDOM}_{340\text{nm}}$, and suspended particles), summer (NO_3^- and PO_4^{3-}), or fall (Cond). Finally, the third category comprises variables whose mean values do not change significantly as a function of water levels ($(K_d(\text{PAR})) \text{ m}^{-1}$ and TURB).

Comparison of data at the decadal scale revealed a clear warming of waters, a significant increase in nitrite-nitrate concentrations, but a significant decrease in phosphate concentrations. These changes confirm the trend observed since 1979 in many Quebec Rivers [34]. Mean concentrations of these chemical parameters in 2006 were higher than standard limits set for river waters by the Ministère de l'Environnement du Québec as compared to those measured in 1994–1996. In order to assess the ecological integrity of rivers in Québec, there is an urgent need for the implementation of a monitoring program which would allow for the development of solutions to reduce the negative impacts of global warming on the functioning and evolution of river ecosystems. We also recommend reinforcing the strict application of existing water quality laws for nitrogen wastes in rural and city areas.

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